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Kinetics of acetic acid synthesis from ethanol over a Cu/SiO₂ catalyst

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ABSTRACT

The dehydrogenation of ethanol via acetaldehyde for the synthesis of acetic acid over a Cu based catalyst in a new process is reported. Specifically, we have studied a Cu on SiO₂ catalyst which has shown very high selectivity to acetic acid via acetaldehyde compared to competing condensation routes. The dehydrogenation experiments were carried out in a flow through lab scale tubular reactor. Based on 71 data sets a power law kinetic expression has been derived for the description of the dehydrogenation of acetaldehyde to acetic acid. The apparent reaction order was 0.89 with respect to water and 0.45 with respect to acetaldehyde, and the apparent activation energy was 33.8 kJ/mol. The proposed oxidation of acetaldehyde with hydroxyl in the elementary rate determining step is consistent with these both. Density Functional Theory (DFT) calculations show the preference of water cleavage at the Cu step sites. In light of this, an observed intrinsic activity difference between whole catalyst pellets and crushed pellets may be explained by the Cu crystal size and growth rate being functions of the catalyst particle size and time.

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1. Introduction

Acetic acid is a bulk chemical which today is produced in amounts exceeding 10 million tons per year worldwide. The established production route has been dominated by the carbonylation of methanol which only relies on fossil sources [1]. In recent years, under the consideration of CO₂ neutrality and independence of fossil sources, the utilisation of biomass for chemical production has regained significant interest. The dehydrogenation of ethanol to acetic acid over Cu catalysts has been known for about a century [2], but ever since the highly selective carbonylation process was discovered the carbonylation route has attracted far the most interest due to its comparably cheap feedstock. Industrially the utilisation of ethanol as a feedstock for acetic acid production has survived the competition from the fossil feedstock based carbonylation process where cheap ethanol is available in large amounts. Less than 10% of the world's capacity of acetic acid is produced according to the route: dehydrogenation of ethanol to acetaldehyde followed by partial oxidation of acetaldehyde to acetic acid [2]. If not carefully operated, however, the two step ethanol route is hampered by a high loss of feedstock to the parasitic CO₂ production in the oxidation step.

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As is well-known, but not industrialised, acetic acid may also be produced from ethanol in a single non-oxidative reaction step [3]. The non-oxidative dehydrogenation of ethanol to acetic acid may be described through the following reactions according to Eqs. (1) and (2).

$CH_3CH_2OH \rightleftarrows CH_3CHO + H_2$	$\Delta H^{\circ} = 68.7 \text{kJ/mol}$	(1)
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 $CH_3CHO + H_2O \rightleftharpoons CH_3COOH + H_2 \quad \Delta H^\circ = -24.8 \text{ kJ/mol}$ (2)

Both reactions are equilibrium limited, implying that unconverted ethanol and acetaldehyde should be separated from the acetic acid product and recycled in an industrial process.

Depending on the catalyst activity the further esterification of ethanol with acetic acid may take place:

$$CH_3CH_2OH + CH_3COOH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$$
(3)

and butanol or other condensation side-products may be produced:

$$2CH_3CH_2OH \rightarrow C_4H_9OH + H_2O \tag{4}$$

Many Cu catalysts, supported or non-supported, are able to convert ethanol to acetic acid. Especially Cr promoted Cu catalysts have been studied due to their regeneration and stabilising abilities, but the carcinogenic effects of Cr in its hexavalent form makes this promoter less desirable. The kinetics of the first conversion (Eq. (1)) has been investigated on unsupported Cu as well as Cr promoted Cu by Tu et al. [4], where it was found that the dehydrogenation of ethanol to acetaldehyde is a first order reaction in ethanol. An apparent activation energy of the non-promoted unsupported Cu

catalyst of 51 kJ/mol was found. However, the data analysis by Tu et al. [4] appears to have been conducted without allow for the fact that the dehydrogenation reaction is equilibrium limited. Herein, it was assumed that the fraction of converted ethanol should be read as the fraction of ethanol converted divided by equilibrium ethanol conversion fraction, which would be the normal parameter subject to graphical analysis with equilibrium reactions. This would explain the high degree of conversion reported for ethanol. The chemical equilibrium for this reaction has been discussed [5,6].

However, in an overall ethanol to acetic acid process high catalyst selectivity to the desired product may be of even greater importance than a high activity, due to simpler product recovery section. We have found that Cu on SiO_2 is a highly selective dehydrogenation catalyst presumably due to its support neutrality, thereby inhibiting e.g. acid or base catalysed dehydration and condensation reactions.

The kinetics for the second conversion (Eq. (2)) on Cu has not been reported to our knowledge. Parts of the pathway and mechanism have been elucidated through conversion of intermediates, surface studies and isotopic labelling [7–11]. Furthermore, support for the mechanisms may be found in similar chemical conversions, where the difference between the reactions is merely the nature of the radical attached to the functional group. Cu catalysts are known to catalyse the dehydrogenation of methanol as well [12-14]; herein C1 is designated as the set of elementary reactions occurring on a Cu surface active in methanol reforming, while C2 has been designated as the set of elementary reactions involved in Cu surface catalysed ethanol reforming. Comparison between part of the C1 and C2 mechanisms on Cu has been suggested [7,8,10]. The C1 mechanisms are interconnecting methanol, water and formic acid in parallel while the C2 mechanisms are interconnecting ethanol, water and acetic acid. The common elementary surface reactions involved in water dissociation on Cu sites have furthermore been discussed [15-17].

In order to support the process development of the new acetic acid process, for example to properly design the synthesis reactors and establish the optimal reaction conditions, a kinetic model is needed. In this paper we have focused on the kinetic order of water and acetaldehyde in the conversion of acetaldehyde with water to acetic acid and hydrogen (Eq. (2)) and the correlations between the Cu crystal size and activity. DFT calculations have been made on the dissociation of water on Cu slabs. A kinetic discussion is made on the basis of mechanistic considerations. A power law expression is used to model the experimental data.

2. Experimental

2.1. Catalyst preparation

The Cu/SiO₂ catalyst used for this kinetic study was prepared by precipitation of Cu(NO₃)₂ with K₂CO₃ in a suspension of HSAsilica (specific surface area = 348 m²/g) at pH 6.0. The precipitate was ripened at 333 K for 1 h, then filtered and washed with hot water until the filtrate had a conductivity of less than 0.1 mS/cm, and finally it was dried at 353 K. The powder (45.7 wt% Cu loading, 0.24 wt% K) was mixed with 3.3 wt% graphite as a lubricant and 5 mm × 6 mm ($h \times d$, height × diameter) cylindrical pellets were made from the catalyst powder, which were then calcined at 623 K for 2 h before use. In part of the experiment a sample of crushed catalyst pellets from a 1–3 mm sieve fraction was used in place of whole pellets.

Different batches of Cu/SiO₂ were made on the same recipe. One sample was used for equilibrium data, one for the prediction of reaction order. The whole pellets all originated from the same batch.

2.2. Catalyst characterisation

Theoretical DFT calculations were made in-house by using a Dacapo calculator on the simulation of a three-layer thick copper slab. The water binding energy was calculated by subtracting the energy of the relaxed copper slab and the water in the gas phase from the total energy of the water adsorbed on the copper slab.

X ray diffraction (XRD) was conducted in an X ray diffractometer with Cu K α 1 radiation of a wave length of 1.54 Å.

In situ reduction was conducted in Transmission Electron Microscope (TEM) on crushed catalyst powder in a Titan ETEM apparatus. The microscope was operated at 300 kV and tuned to a flat information transfer out to 20 mrad using the supporting SiN membrane window before conducting the experiment. The hydrogen source was Alphagas H_2 . Imaging took place before and during exposure to app. 10 mbar H_2 at 608 K.

An EXAFS study on *in situ* reduction of a 100–150 micron sieve fraction of the crushed catalyst was conducted at the beamline X1 at HASYLAB. QEXAFS scans were recorded using a Si(111) doublecrystal monochromator in continuous screening mode between 8500 and 9700 eV. The energy was calibrated using a Cu foil. The data were reported on an *in situ* cell as described in reference [18] and background removal and data fitting were conducted with the Win XAS software [19].

2.3. Catalyst testing

Dehydrogenation of ethanol mixtures was conducted in an 8 mm reactor tube installed in a ventilated temperature controlled oven. The catalyst was loaded either as (a) whole pellets (12 g cylindrical $h \times d$: 5 mm \times 6 mm) in a single-pellet-string configuration with 3 mm glass balls as separators or (b) as crushed pellets (4 g, 1-3 mm sieve fraction) diluted with SiC in a 1:1 ratio on volume basis. The catalyst was activated in each case prior to the experiment with 5% H₂ in N₂ at 523 K and a flow rate of 900 Nml/min for 7 h. The liquid reactant was fed by means of a high precision pump (HPLC pump, LDC Analytical, ConstaMetric 3200) to an evaporator installed inside the ventilated oven. Preheated N₂ carrier gas was added from a mass flow controller at a ratio of either 333 or 666 Nml per ml of liquid feed to the evaporated feed before being introduced to the reactor. The inlet temperature and the reactor wall temperature were the same. The molar feed ratios of ethanol to water in the liquid feed were 60:40, 50:50, 40:60 and 20:80. In addition, 10% of an acetaldehyde and water mixture in a 50:50 molar ratio was co-fed in some experiments. The temperatures ranged from 553 to 613 K and the operating pressure was slightly above atmospheric.

The liquid products were sampled in a condenser cooled to 258 K by a cooling circuit. The gas flow rate at the exit of the condenser was measured by means of a flow meter and the condensate flow rate was calculated. Online GC was not obtainable due to the corrosivity of the product, potentially damaging the sample port (previous experience). The composition of the condensate was determined by means of a gas chromatograph (GC) with a flame ionisation detector (FID). Based on the measured composition and the assumption that acetaldehyde would be the only condensable escaping the condenser in significant amounts (established by analysis), a complete calculated mass balance could be established. The water and the acetic acid concentration in the condensate were double checked by titration.

Due to the hard to handle acetaldehyde the variation of acetaldehyde vs. water in the feed was in most cases obtained indirectly by feeding ethanol and water in different ratios, having observed that the dehydrogenation reaction of ethanol to acetaldehyde (Eq. (1)) is much faster than the dehydrogenation of acetaldehyde (Eq. (2)).

Minute side products (<0.2 mol%) count ethyl acetate, diethoxy ethane and ppm concentrations of n-butanol. All the unloaded cat-

alyst samples were analysed by means of XRD. The samples were passivated in $1\% O_2/99\% N_2$ at room temperature before unloading.

For each series of kinetic experiments carried out on whole pellets for a given feed composition the temperature and flow rates were varied to provide kinetic data at varying contact times, and at each temperature the first flow rate was repeated in the end before changing the temperature in order to follow the deactivation of the catalyst. Each data point was compensated for deactivation assuming that the rate equations of both Eqs. (1) and (2) were influenced to the same degree, based on the Eq. (2) activity. The degree of deactivation was 0–50% dependent on temperature.

The resulting kinetic data sets comprise numbers for feed and effluent compositions, catalyst mass, inert mass, reactor length, temperature, pressure and flow rate. To include thermal transport effects and efficiently combine the analysis of the two consecutive conversions according to Eqs. (1) and (2) the kinetic data obtained were evaluated based on the data sets by contemporary integration in a one-dimensional wall cooled plug flow reactor model on the suggested power-law kinetics. The one-dimensional reactor software is developed in-house but in principle any one-dimensional reactor modelling software with appropriate integration accuracy may be used for this purpose. With the above mentioned one-dimensional reactor model it was possible to perform integration over the catalyst mass for each of the experiments, $n = 1, 2, 3, ..., N_{exp}$, where N_{exp} is the total amount of proper experiments, thereby calculating the product outlet concentrations.

An error function was defined with respect to all the data sets evaluated and to both the acetaldehyde and the acetic acid outlet concentrations in the individual data sets. The error function (Eq. (5)) expresses the sum of the squared sum of the relative deviation between the calculated outlet concentrations, y_{calc} , of acetaldehyde and acetic acid according to Eqs. (1) and (2) and the corresponding measured concentrations, y_{exp} , at the outlet of the reactor.

$$SSQ = \sum_{n=1}^{N_{exp}} \left(\sum_{i=HAc, HOAc} \frac{y_{calc,i} - y_{exp,i}}{y_{exp,i}} \right)^2$$
(5)

By means of the Complex Box method and by varying the kinetic coefficients and activation energies in the suggested kinetic expressions used for calculating the outlet concentrations, a minimisation of the error object function value and a set of the correspondingly optimised variables were obtained.

3. Results

3.1. Catalyst characterisation results

XANES and EXAFS showed that the reduction of the CuO in the fresh catalyst sample the Cu/SiO₂ catalyst started at 488 K and was finalised at 510 K. Fig. 1 shows a selection of the EXAFS spectra recorded during the *in situ* reduction of the test sample.

Obviously complete reduction of Cu(II) to Cu (0) is obtained within a narrow temperature window leaving copper in its metallic state.

The formation of Cu particles on the surface of the SiO₂ support upon activation is supported by the analysis of the TEM images. Fig. 2 shows the Cu crystals formed on the SiO₂ surface when subjected to 11 mbar H₂ at 608 K.

Further investigation of the Cu crystal size by XRD (Scherrer equation) showed that substantially larger Cu crystals were formed on the whole pellets during reduction (160 Å compared to 110 Å on crushed pellets). Likewise the growth rate of the Cu crystals seems to be influenced by the size of the catalyst particle. Sintering due to water formed during reduction may be the explanation for the larger Cu crystals found on the whole pellets. Fig. 3a shows the size



Fig. 1. EXAFS spectra obtained during *in situ* reduction of 50 mg 100–150 micron sieve fraction Cu/SiO₂ catalyst in 5% H_2 (flowing at a rate of 10 Nl/(min g)) at room temperature (298 K, RT), 488, 498 and 579 K. The spectrum at 579 K corresponds to Cu(0).

of the Cu crystals along the [200] direction (Cu D[200]) just after reduction, Fig. 3b shows an XRPD spectrum for a specific catalyst sample, and Fig. 3c shows the initial acetic acid formation rate of whole catalyst pellets compared with crushed catalyst pellets. Further sintering was observed after a number of hours on stream for whole pellets and crushed catalyst pellets.

In-house DFT calculations show that water preferably dissociates on Cu(211) surfaces, or step sites, the density of which decreases with the Cu particle size. The Cu(211) surface calculations give an energy barrier of 1.3 eV (125 kJ/mol) for the water dissociation reaction.

3.2. Pathway and equilibriums

In order to establish the pathways and equilibriums of the reaction system of Eqs. (1) and (2) a reaction profile experiment was initially made at high to very low liquid weight hourly space velocities, LWHSV (g/(gh)), expressing the load of liquid feed per time unit on the catalyst mass.

Fig. 4 shows the reaction profile found for the conversion of a feed mixture with the molar ratio of ethanol to water of 40:60.

The concentration profile in Fig. 4 (ethanol = EtOH, water = H_2O , hydrogen = H_2 , acetaldehyde = HAc, acetic acid = HOAc) with acetaldehyde going through a maximum confirms acetaldehyde as a typical intermediate. As may be gathered, the reaction rate of the



Fig. 2. TEM image showing Cu crystals of average size>100 Å (dark circular) on SiO₂ support (brighter shades) after *in situ* reduction at 335 $^{\circ}$ C in 10.5 mbar H₂.



Fig. 3. (a) The Cu crystal size D[200] analysed by *ex situ* XRPD after reduction and operation. The resulting Cu crystal size depends on the catalyst particle size and time on stream. HOS is hours on stream. (b) An *ex situ* XRPD for a 1.4 mm Cu/SiO₂ catalyst particle reduced in 5% H₂ and operated for 61 h on a 40:60 ethanol/water molar feed diluted to 50% by nitrogen. (c) Arrhenius plot of the initial rates of acetic acid formation vs. inverse absolute temperature for a 40:60 ethanol/water feed.

dehydrogenation reaction of ethanol (Eq. (1)) is much faster than the dehydrogenation of acetaldehyde with water to acetic acid and hydrogen (Eq. (2)). Furthermore, the profile seems to level out at low LWHSV, indicating that the equilibrium is approached. In a kinetic evaluation the reaction rate is typically corrected with $(1 - \beta)$ for considering a reaction approaching equilibrium, if it describes a first order conversion, where β is the reaction quotient divided by the corresponding equilibrium constant. Therefore, the equilibrium temperature function had to be estimated for this purpose.

The approximate reaction quotient, Q_{appr}, may be expressed as:

$$Q_{appr} = \frac{p_{H_2} \cdot p_{CH_3CHO}}{p_{CH_3CH_2OH} \cdot p^{\theta}}$$
(6)



Fig. 4. The reaction profile of a 40:60 ethanol/water mixture diluted with N₂ to 50 mol% fed into a bed of crushed Cu/SiO₂ catalyst at an outlet temperature of 588 K at close to atmospheric pressure. Minor side-products e.g. ethyl acetate and n-butanol have been neglected in the figure. The concentrations (mol%), of the acetaldehyde (HAc) and acetic acid (HOAc) products may be found on the right abscissa.

where p_{H_2} , $p_{CH_3CH_0}$ and $p_{CH_3CH_2OH}$ are the partial pressures of hydrogen, acetaldehyde and ethanol, respectively, and p^{θ} is the gas standard state pressure (1.013 bar = 1 atm). At low LWHSV the approximate reaction quotient as calculated by Eq. (6) for the smoothed data at 588 K is about 0.7, at a total operating pressure of 1.05 bar.

The degree of conversion of acetaldehyde with water to acetic acid and hydrogen according to Eq. (2) was in all kinetic experiments so low that the reaction was far from equilibrium.

Feeding a mixture of acetaldehyde, being an intermediate, and water to the catalyst gave no ethyl acetate side-product, while acetic acid was produced, and the production rate of acetic acid was higher than if a mixture of ethanol and water was used as a feed. The result indicates that acetic acid may be produced directly from acetaldehyde and water, and that this is the primary route to acetic acid from ethanol and water.

3.3. Kinetic modelling

While the differential reactor type is the most preferred for kinetic investigations, sound approaches may be obtained also through integral reactors as long as a broad range of low to high degrees of conversions are obtained for a variation of feeds at different temperatures. With two consecutive reactions and minor side-reactions taking place, the smoothest analysis is obtained by using computer modelling. The reaction rate according to the reaction in Eq. (2) is so low that diffusion limitation is not controlling the observed rates even on whole catalyst pellets of the size used in our experiments. In such case, the application of a single-pellet string reactor type is favourable in that the reactor may be modelled more easily [20]. With a limited reactor volume and a slow reaction in question the degree of conversion would be too low for modelling of crushed catalyst at realistic ethanol partial pressures.

By applying a data fitting program using a non-linear optimisation method on the sum of squared relative errors between the observed and modelled product concentrations the kinetic parameters may be fitted.

Present experiments were conducted at initial ethanol partial pressures 0.11–0.26 bar and water partial pressures 0.18–0.45 bar. Acetaldehyde was in some cases co-fed at an initial partial pressure of 0.05 bar. In order to investigate its influence on the acetic acid formation rate the acetaldehyde partial pressure at low contact time



Fig. 5. Log–log plots of the acetaldehyde space-time yield (STY) vs. the average ethanol concentration and the acetic acid STY vs. the average water concentration, respectively, at 563 K and atmospheric pressure as a simple approach for determining the reaction orders in the kinetic expressions for Eqs. (1) and (2) for crushed pellets. Averages are arithmetic inlet to outlet.

was further varied indirectly by varying the initial ethanol partial pressure. The temperature was varied between 553 and 613 K.

3.3.1. Crushed catalyst pellets

As mentioned above, the operation of the experimental reactor at close to isothermal conditions may be obtained with a bed of crushed catalyst pellets diluted with SiC, which has high thermal conductivity, 360 W/mK. Such experiments were conducted in order to observe the reaction order effects while minimising the effect of non-isothermal behaviour.

In one part of the experiment – on crushed catalyst – the ethanol/water ratio was fixed while its feed rate was changed keeping the nitrogen carrier gas flow rate and the temperature constant. Hereby, the partial pressures of the water and ethanol feed were changed, while the exit acetaldehyde concentration was almost constant.

The influence of the two varied reactants was investigated by plotting the space-time yields (STYs) of the products vs. the average of the reactants concentration log–log in a series of experiments conducted at 563 K, where the degree of conversion is rather low, hereby approaching differential analysis. Fig. 5 shows the plots to determine the reaction order of Eq. (1) with respect to ethanol and the reaction order of Eq. (2) with respect to water.

An approximation of the reaction order of the first rate equation (Eq. (1)) with respect to ethanol was obtained as the slope of the log–log depiction of the acetaldehyde STY, STY HAc, vs. the average ethanol concentration (arithmetic inlet to outlet) in vol%. The STY HAc value includes the amount of acetaldehyde which had further been converted to acetic acid. The reaction order with respect to ethanol is found to be 0.8 by this analysis. Apart from not being an actual but rather an average reaction rate, the STY does not compensate for the approach to equilibrium. β for Eq. (1) ranged from 0.05 to 0.15.

In the study by Tu et al. [4] conducted at 523–583 K the conversion of ethanol to acetaldehyde was found to take place according to a first order reaction in ethanol. Based on this literature evidence and the above finding, the rate equation for the dehydrogenation of



Fig. 6. The modelled conversions and the radial averaged temperature (lines) and the experimental values for acetaldehyde (square) and acetic acid (cross); *y* is indicated in mol%. The partial pressure of ethanol = 0.26 bar and the partial pressure of water = 0.39 bar in the feed. The feed/wall temperature = 573 K.

ethanol to acetaldehyde (Eq. (1)) was assumed to be of first order in ethanol in the further data analysis.

According to the same method and based on the same data the log–log plotting of the STY of acetic acid, STY HOAc, vs. the average water vol% was made (Fig. 5) in order to indicate the reaction order with respect to water in Eq. (2). As mentioned above, during these experiments the acetaldehyde concentration in the effluent was almost constant. If as an approximation the acetaldehyde concentration profile is assumed constant in this series of experiments, we find a reaction order of water of 1.05, i.e. a close to first order dependence.

3.3.2. Whole pellets

Modelling an example of a conversion profile based on a first order reaction rate for Eq. (1) confirms that isothermal operation is not achieved. Fig. 6 shows the modelled conversion and temperature profiles for an example, where *y* is the concentration of acetaldehyde and acetic acid in mol%, respectively.

However, by means of the fact that Δt approaches 0 at low contact times the initial rates, r_{ini} , defined as the reaction rate of the feed composition of acetic acid formation for an infinitely low concentration of acetaldehyde may approximately be established from the depiction of y_{HOAc} vs. 1/SV irrespective of the non-isothermal behaviour. The r_{ini} values are found as the tangent slopes in 1/SV = 0.

Fig. 7 shows the log–log plot of experimental results of a series of feeds on whole pellets where the ethanol partial pressure was kept constant while the water partial pressure was varied. In effect, this variation of water partial pressure at constant ethanol implies a constant acetaldehyde concentration at a given, low contact time, as the Eq. (1) reaction rate is very high and is assumed being dependent on ethanol alone.

Note that both on crushed and sieved catalyst and whole catalyst pellets the reaction order of water is close to 1.

In a further series of experiments acetaldehyde was co-fed leading to a remarkable increase of the initial reaction rate to acetic acid. Therefore, overall a rate expression for Eq. (2) is suggested depending on both water, with a close to first order dependence, and acetaldehyde partial pressures.

3.4. Parameter fitting

As mentioned, the conversion of ethanol to acetaldehyde was assumed to be a first order reaction with respect to ethanol. The



Fig. 7. The initial acetic acid formation rate vs. the partial pressure of water at toven = 573 K and constant ethanol pressure (0.26–0.265 bar) in the feed on whole catalyst pellets.

power law expression in accordance herewith may be expressed as follows:

$$-r_{\mathrm{CH}_{3}\mathrm{CH}_{2}\mathrm{OH},1} = A_{1} \cdot \exp\left(\frac{-E_{1}}{RT}\right) \cdot p_{\mathrm{CH}_{3}\mathrm{CH}_{2}\mathrm{OH}} \cdot (1-\beta_{1})$$
(7)

where A_1 is the pre-exponential factor in mol/(g h bar), E_1 is the apparent activation energy in kJ/mol, $p_{CH_3CH_2OH}$ is the partial pressure of ethanol in bar, and β_1 is the observed reaction quotient divided by the equilibrium constant for Eq. (1).

Even with a certain reduction of the reaction rate due to diffusion limitation, the order of the reaction remains 1.

The reaction according to Eq. (2) was given a power law rate equation, with a dependence of acetaldehyde and water:

$$-r_{\text{CH}_3\text{CH}_0,2} = A_2 \cdot \exp\left(\frac{-E_2}{RT}\right) \cdot p_{\text{CH}_3\text{CH}_0^{\gamma}\text{CH}_3\text{CH}_0} \cdot p_{\text{H}_20^{\gamma}\text{H}_20} \cdot (1-\beta_2)$$
(8)

where A_2 is the pre-exponential factor in mol/(g h bar^{$\Sigma\gamma$}), E_2 is the apparent activation energy in kJ/mol, p_{CH_3CHO} is the partial pressure of acetaldehyde in bar, p_{H_2O} is the partial pressure of water in bar, γ_{CH_3CHO} and γ_{H_2O} are the reaction orders with respect to acetaldehyde and water, and β_2 is the observed reaction quotient divided by the equilibrium constant for Eq. (2). The approach to equilibrium expressed by β_2 was in all cases almost negligible.

Using a one-dimensional reactor modelling program the above power law expressions were evaluated.

In the rate expression, Eq. (7), the pre-exponential factor, A_1 , and the apparent activation energy, E_1 , were allowed to vary, while in the rate expression, Eq. (8), both the pre-exponential factor, A_2 , the apparent activation energy E_2 and the exponents, γ_{CH_3CHO} and γ_{H_2O} , were defined as variables.

The optimised parameters found for the 71 data sets with ethanol partial pressures 0.11-0.26 bar, water partial pressures 0.18-0.45 bar and acetaldehyde co-fed at up to 0.05 bar, diluted with N₂ carrier gas, and the temperatures ranging from 553 to 613 K, were as follows:

$$A_1 = 3.53E_3 \text{ mol}/(\text{g h bar})$$
 $E_1 = 43.7 \text{ kJ/mol}$

 $A_2 = 20.4 \text{ mol}/(\text{g h bar}^{1.34})$

 $\gamma_{CH_3CHO} = 0.45$ $\gamma_{H_2O} = 0.89$ $E_2 = 33.8 \text{ kJ/mol}$

Fig. 8 shows the parity plots for acetaldehyde and acetic acid respectively sorted in 3 selected reactor wall/inlet temperatures.



Fig. 8. Parity plots of calculated vs. measured concentration of the products acetaldehyde and acetic acid based on whole catalyst pellets. Upper: acetaldehyde. Lower: acetic acid. The plot points are sorted in three series corresponding to the reactor wall/feed temperature: diamonds 553 K, filled squares 573 and crosses 593 K.

The objective here was to study the kinetics for the conversion of acetaldehyde with water to acetic acid and hydrogen. As shown above in Fig. 6, the reactor was not operated completely isothermally. The integral analysis of the two rate expressions, Eqs. (7) and (8), was however accounting also for the actual temperature profile in the test reactor. From above parity plots Fig. 8 it is seen that no systematic deviation occurs with reactor wall/feed temperature variation. This indicates a good validity of the apparent activation energy found for the studied conversion kinetics.

For comparison, further kinetic data as to conversion, selectivity and stability of the Cu/SiO₂ catalyst are enclosed in Appendix A.

4. Discussion

4.1. Side-reactions and equilibrium

Using the present Cu/SiO_2 catalyst, only very limited sidereaction conversion to ethyl acetate and butanol via Eqs. (3) and (4) have been observed for the catalyst tested. In literature such side-products are typically reported [7,9].

At higher temperatures the ethanol may dehydrate to ethylene [21]. However, no such side-production of ethylene was observed in the temperature range 553–613 K.

Regarding the ethanol dehydrogenation (Eq. (1)), the approximate reaction quotient value of about 0.7 was found in present investigation at 588 K for low LWHSV, approaching equilibrium. This value corresponds closely to the equilibrium constant of 0.8 at 588 K obtained theoretically from the Stull et al. [5] thermochemical values as calculated by Happel et al. [6]. Happel argues that the departure from ideal behaviour is insignificant for Eq. (1) at the conditions given allowing the direct comparison of the approximate reaction quotient (Eq. (6)) at low LWHSV with the equilibrium constant value. The corresponding standard entropy and enthalpy of formation of acetaldehyde proposed by Stull et al. [5] are 264.2 J/(mol K) and -166.4 kJ/mol. Happel et al. [6] made a series of experiments based on the approaching of the Eq. (1) equilibrium from both sides at temperatures 456-533 K. They compared their own experimental values against various literature thermochemical and experimental data for this reaction. Happel et al. [6] also found that their equilibrium data agreed best with the thermodynamic values reported by Stull et al. [5]. These standard entropy and enthalpy values for acetaldehyde were therefore used in our data evaluation.

4.2. Mechanism

Up to now no kinetic model, empirical or microkinetic, for the conversion of acetaldehyde to acetic acid has been suggested in the literature. But some of the elementary steps have been reported. From one side it is difficult to determine a mechanism from an empirical kinetic expression. The other way round with some mechanistic information it gets easier to propose an empirical expression with greater validity. Reference is made to the Appendix B where mechanistic considerations are made based on the literature [7–13], comprising the corresponding C1 mechanisms. Appendix B also contains Table 1 showing the considered elementary reaction steps I–XVII on the Cu surface. Reference to these steps I–XVII in Table 1 are hereinafter made directly.

As learned in Appendix B, the formation of CH_3CHOO^* may, with a basis in the C1 elementary steps, be explained through the oxidation of an adsorbed acetaldehyde with adsorbed O*, step VIII or adsorbed OH* to H* and CH_3CHOO*, step IX, or it may be explained through a direct ethoxy route: ethanol dissociation into adsorbed ethoxy and H*, the ethoxy being oxidised with adsorbed O* to CH_3CHOO* and adsorbed H*, see steps I, II+VII. The CH_3CHOO* then abstracts α -hydrogen, step X, and the acetate formed reacts with adsorbed hydrogen to acetic acid which desorbs, steps XI–XII.

Adsorbed oxygen or hydroxyl needed for these oxidations may be obtained by the dissociation of adsorbed water to OH* and H* on the Cu surface, followed by 2 adsorbed hydroxyls forming adsorbed water and atomic oxygen, steps XIII–XVI. Dihydrogen gas is formed by desorption of two adsorbed hydrogen, step XVII. The dissociation of water, step XIV, is known to be slow [13] and rate determining under typical water-gas shift conditions.

Accordingly, the reaction mechanism of ethanol dehydrogenation with water to acetic acid and hydrogen via acetaldehyde (Eqs. (1) and (2)) may be described through the discussed elementary steps of steps I–XVII.

4.3. Rate determining step

The dissociation of water on Cu surfaces (step XIV) is known [13] to be rate determining under typical water gas shift conditions in conjunction with the methanol reforming, C1 system.

We may note, however, that whereas a high activation barrier (84 kJ/mol) for the dehydrogenation of formaldehyde into formyl is predicted by Shustorovich [14] for the C1 system, the ready formation of adsorbed acetyl CH₃CO* from acetaldehyde was observed in the C2 system on a Cu surface [11].

Furthermore, it is reported by Iwasa and Takezawa [7] that in the C1 system the dehydrogenation step of methanol to formaldehyde is rate determining over its further conversion to methyl formate or carbon dioxide, via formate. For the C2 system the dehydrogenation step to acetaldehyde is much faster than its further steps to acetic acid.

As the formation rate of acetic acid is higher from acetaldehyde than from ethanol, the alternative overall ethoxy route via step VII seems to not be the dominant. It is likely that the rate determining step is either of the oxidations in step VI, step VIII or step IX, or the dissociation of water, step XIV. Either which oxidant, O* or OH*, reacts with adsorbed acetaldehyde or acetyl, water must dissociate via elementary step XIV on the Cu surface to provide for these.

4.4. Reaction order

In analysing the Langmuir–Hinshelwood type reaction rate expressions for a proposed rate determining step, the denominator term $(1+\sum$ adsorption terms) expresses the reduction of activity due to occupation of free sites by adsorbed species. Askgaard et al. [12] report that the coverage of the free Cu sites in the C1 system highly depends on the pressure of the active components. At 2 bar and 500 K the relative abundance of free sites is 0.88,

Table 1

Elementary reaction steps suggested for the dehydrogenation of ethanol via acetaldehyde to acetic acid on Cu, steps VII–XI based on C1 elementary reactions on Cu. * signifies a free Cu site.

	Elementary surface reaction	Туре	Reference
Ι	$CH_3CH_2OH(g) + * = CH_3CH_2OH^*$	Ethanol adsorption	[8,11]
II	$CH_3CH_2OH^* + * = CH_3CH_2O^* + H^*$	Hydroxyl hydrogen abstraction	[8,11]
III	$CH_3CH_2O^* + * = CH_3CHO^* + H^*$	Ethoxy α -hydrogen abstraction	[8,11]
IV	$CH_3CHO^* = CH_3CHO(g) + *$	Acetaldehyde desorption	[7,8,11], this work
V	$CH_3CHO^* + * = CH_3CO^* + H^*$	Acetaldehyde α -hydrogen abstraction	[11]
VI	$CH_3CO^* + OH^* = CH_3COOH^* + *$	Acetyl hydroxyl oxidation	[11]
VII	$CH_3CH_2O^* + O^* = CH_3CHOO^* + H^*$	Ethoxy oxidation	[12]
VIII	$CH_3CHO^* + O^* = CH_3CHOO^* + *$	Acetaldehyde oxidation	[12]
IX	$CH_3CHO^* + OH^* = CH_3CHOO^* + H^*$	Acetaldehyde hydroxyl oxidation	[12]
Х	$CH_{3}CHOO^{*} + * = CH_{3}COO^{*} + H^{*}$	Acetate formation	[12]
XI	$CH_{3}COO^{*} + H^{*} = CH_{3}COOH^{*} + *$	Acetic acid formation	[12]
XII	$CH_3COOH^* = CH_3COOH(g) + *$	Acetic acid desorption	[7,12], this work
XIII	$H_2O(g) + * = H_2O^*$	Water adsorption	[7,12,16,17]
XIV	$H_2O^* + * = OH^* + H^*$	Water dissociation	[7,12,16,17]
XV	$20H^* = H_2O^* + O^*$	Hydroxyl disproportionation	[7,12,16,17]
XVI	$OH^* + * = O^* + H^*$	Hydroxyl dissociation	[7,12,16,17]
XVII	$2H^* = H_2(g) + 2^*$	Dihydrogen formation	[7,12,16,17], this work

balanced primarily by coverage of adsorbed hydrogen. It may be argued then that at 0.5 bar of reactants and products and 553 K, i.e. four times lower pressure and a higher temperature, the free sites are by far the most abundant species. Assuming that the free sites are dominant, the adsorption terms become negligible, leaving basically a rate equation equal to the numerator term of the full Langmuir–Hinshelwood expression.

Whereas the conversion of acetaldehyde to acetic acid is rather slow the dehydrogenation of ethanol to acetaldehyde is so fast that pore diffusion limitation could influence the observed rate. Being a first order reaction intrinsically one would, however, still expect a first order behaviour in ethanol for the ethanol dehydrogenation under the influence of pore diffusion limitation, the observed activation energy being somewhat lower, depending on the pore branching.

We find an observed activation energy of 44 kJ/mol for the ethanol dehydrogenation, Eq. (1). Tu et al. finds an intrinsic activation energy for ethanol dehydrogenation to acetaldehyde on pure Cu of 51 kJ/mol. The two values are basically consistent keeping in mind that our value is slightly lowered due to the diffusion limitation in our whole pellet experiments. Shustorovich and Bell [14] calculates the activation energy barrier of the formation of methoxy from adsorbed methanol to be around 38 kJ/mol. The energy of hydrogen abstraction from ethanol should be similar; thus the calculated value by Shustorovich and Bell is consistent with the activation energies for Eq. (1) found experimentally.

The approximate determination of the apparent reaction order of 0.8 (see Fig. 5) in ethanol is consistent with the finding by Tu et al. [4] who report the reaction order with respect to ethanol to be 1.

Guan and Hensen [15] investigated the ethanol dehydrogenation on a silica supported gold catalyst. The reaction rate was found to be solely first order with respect to ethanol. The first order ethanol dependence without the dependence of hydrogen is consistent with a Langmuir–Hinshelwood expression with negligible adsorption terms assuming that the first hydrogen abstraction is the rate determining step [22].

For the acetaldehyde conversion, Eq. (2), we find an apparent reaction order of water close to unity. However, a dependence of acetaldehyde was found as well. A reaction order for the reaction in Eq. (2) close to unity for water (see Fig. 5) may reflect that the elementary step XIV is rate limiting. Under this assumption, a reaction order higher than 0 with respect to acetaldehyde reflects that the dissociation of acetaldehyde or acetyl. However, the dissociation energy of adsorbed water on step sites was found to be 125 kJ/mol by means of DFT calculations, which is far from the apparent activation energy 34 kJ/mol as found experimentally for Eq. (2). Wang et al. have reported water dissociation energies of 100-123 kJ/mol for the Cu(110), Cu(100) and Cu(111) surfaces [23]. Due to this discrepancy, we do not believe that water dissociation is the rate limiting step in Eq. (2).

Colley et al. found that the activation energy for the dehydrogenation of adsorbed acetaldehyde to acetyl is much smaller than the desorption of acetaldehyde leading to low concentrations of acetaldehyde in the gas phase. We do, however, see very high concentrations of acetaldehyde in our reaction system where adsorbed acetaldehyde or acetyl possibly reacts with dissociated water, O* or OH*. This indicates that the acetaldehyde or acetyl oxidations (Table 1, steps VI, VIII or IX) have considerable activation barriers. Therefore, it is most likely that either the oxidation with O* or OH* of adsorbed acetaldehyde or hydroxyl oxidation of acetyl is rate determining.

The assumption of acetaldehyde or acetyl oxidation being the rate determining step does indeed result in a Langmuir–Hinshelwood expression, based on one site type, where the observed numerator has a reaction order of 1 both with respect to water and acetaldehyde. Furthermore a reaction order with respect to hydrogen of $-\frac{1}{2}$ is found assuming acetaldehyde oxidation with adsorbed hydroxyl, OH*, to be rate determining, while the hydrogen reaction order was found to be -1 for acetaldehyde oxidation with atomic oxygen, O*, or acetyl oxidation with adsorbed hydroxyl as the rate determining step, respectively.

Elementary steps XIII–XVII were studied on a Cu[111] surface by Phatak et al. [16] and it was found that the coverage of OH* is a factor of 10^6 as high as the O* coverage. In a more recent study by Chen et al. [17] it was found that hydroxyl even binds stronger on Cu[321] step sites. Therefore, most likely the oxidation takes place by means of adsorbed hydroxyl, OH*.

As mentioned, the intrinsic reaction rate model has hydrogen dependence as well. Hydrogen was varied as a process parameter however being proportional to the acetaldehyde partial pressure in most cases. Assuming that the rate determining step is the oxidation of adsorbed acetaldehyde with hydroxyl, the corresponding Langmuir–Hinshelwood expression may explain the observed near 0.5 dependence of acetaldehyde if the apparent reaction order reflects in reality an overall acetaldehyde and hydrogen dependence and if the adsorption terms are truly negligible. Eq. (9) expresses the forward Langmuir–Hinshelwood reaction rate for Eq. (2) being far from equilibrium, based on the above assumption.

$$-r_{\text{CH}_{3}\text{CHO},\text{L}-\text{H},\text{forward}} = \frac{k \cdot (p_{\text{H}_{2}\text{O}} \cdot p_{\text{CH}_{3}\text{CHO}})/p_{\text{H}_{2}}^{1/2}}{(1 + \sum \text{adsorption}_{\text{terms}})^{2}}$$
(9)

where *k* is the resulting apparent rate constant and p_{CH_3CHO} , p_{H_2O} , p_{H_2} are the partial pressures of acetaldehyde, water and hydrogen.

Assuming the pathway would go through acetyl oxidation with hydroxyl, the overall acetaldehyde and hydrogen reaction order of the numerator alone is 0, which does not correspond well with the overall dependence of acetaldehyde and hydrogen found by optimisation.

Furthermore, a positive dependence of the total pressure would be expected from any of these terms. However, increasing the operating pressure by a factor of 10 caused serious deactivation of the catalyst, presumably due to sintering, so this information was veiled by an overlaying deactivation phenomenon.

The dependence in acetaldehyde (and hydrogen) could thus be explained by the oxidation of adsorbed acetaldehyde with hydroxyl as the primary pathway and the rate determining step, in agreement with the suggestion by Iwasa and Takezawa [7]. Citing Ovesen et al. [13] different mechanisms can lead to the same overall kinetic expression. But based on more indications, the two most likely pathway candidates finally down-selected actually have different reaction order sets, of which one set has a superior fit with the power-law expression found. Best consistence is therefore found for acetaldehyde oxidation with hydroxyl.

The validity of the derived power-law rate equation for the conversion of acetaldehyde (Eq. (8)) may be limited to feeds with approximately equimolar amounts of acetaldehyde and hydrogen.

4.5. Reduction influence

As mentioned, in aiming for more isothermal operation some experiments were conducted on crushed catalyst under which conditions the catalyst seemed to have a 3 times higher intrinsic activity for the conversion of acetaldehyde to acetic acid. The discrepancy cannot be explained by diffusion limitation, as judged from the observed reaction rate, reaction order and the apparent activation energy for the two catalyst sizes tested.



Fig. 9. (a) STY_{HOAC}, (b) ethanol conversion and (c-f) product selectivities vs. time on stream for reaction conditions LWHSV = 0.4–0.5 g/(g h) for a 40:60 ethanol:water feed at t_{bed} = 290–300 °C.

Using the information from the DFT calculations on Cu surfaces the cleavage of water primarily takes place on step sites. According to Guan and Hensen [15], studying dehydrogenation of ethanol on gold surfaces, the density of step sites is expected to depend inversely on the particle size above a certain optimum nanoparticle size; and for constant Cu amount the Cu surface area also depends inversely on Cu crystal size.

Above best consistence with experiments was found for acetaldehyde oxidation with hydroxyl as the rate determining step, having a high dependence of water in the corresponding rate equation. If Cu step sites are the predominant active sites for the cleaving of water the primary coverage of hydroxyl species used in the oxidation of acetaldehyde is also on the step sites. The almost doubling of the Cu crystal size may then, together with the inverse dependence of the density of Cu step sites, account for the reduction of the reaction rate with a factor of 3.

The XRD on the catalyst reveal that the catalyst is influenced by a sintering phenomenon during reduction such that Cu crystals of almost double size are obtained for whole pellets as compared to crushed pellets (1–3 mm sieve fraction). Similarly, the growth rate during operation is affected but the most predominant effect is induced under reduction. It may be argued that reduction water plays a role.

5. Conclusion

Cu/SiO₂ is a selective and well-suited catalyst for acetic acid synthesis from ethanol, the Cu being present as metallic copper particles on the silica support as confirmed by TEM, EXAFS and XRD. DFT calculations show the preferential cleavage of water at Cu step sites.

The reaction quotient of 0.7, approximating the equilibrium constant, at 588 K for ethanol dehydrogenation to acetaldehyde and hydrogen was found to agree well with the equilibrium constant value estimated from the thermochemical data reported by Stull et al. [5].

The suggested reaction order of 1 with respect to ethanol for the dehydrogenation of ethanol to acetaldehyde was supported by the experiments in present study. The apparent activation energy of the non-intrinsic kinetic expression for dehydrogenation of ethanol to acetaldehyde is as expected slightly lower than the intrinsic value reported in literature for pure Cu.

An intrinsic empirical kinetic power law expression for the dehydrogenation of acetaldehyde to acetic acid was derived. The apparent reaction order of water close to unity and the apparent reaction order of acetaldehyde and hydrogen overall of 0.45 tentatively suggest that hydroxyl based oxidation of acetaldehyde can be the rate determining step.

The relationship between the Cu crystal size and the intrinsic activity found is consistent with the suggestion of the hydroxyl oxidation as the rate determining step, and the preferential cleaving of water on step sites as found by DFT.

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Appendix A.

In this appendix we provide further considerations on the experimental basis and some additional catalytic data.

In a first round, the Cu/SiO₂ catalyst was tested as crushed pellets sieve fraction diluted with SiC in order to establish as close to isothermal as possible conditions for equilibrium experiments. However, running on crushed catalyst results in low particle Reynolds Number (Re_p) down to 10 (Re_p = $d_h G/\mu$, where d_h is the hydraulic diameter, *G* is the gas mass velocity per cross section of empty tube and μ is the fluid viscosity) in the 8 mm reactor with the catalyst mass and flow rate limitations given. Therefore, due to the dependence on proper modelling most of the kinetic experiments were conducted with whole pellets in a single-pellet string configuration at Re_p \approx 60–250, making a modelling of the conversion reasonably trustworthy. Furthermore, from the observed reaction rate of acetaldehyde conversion to acetic acid (based on the Weisz–Prater Modulus) no significant internal diffusion limitations are expected.

Fig. 9a–f shows the activity (STY), conversion and product selectivity vs. hours on stream for whole pellets.

Appendix B.

In this appendix we have a discussion on the suggested reaction mechanisms based on literature findings.

As to the reaction pathway Inui et al. [9] suggest that over a Cu–Zn–Zr–Al–O catalyst acetic acid is produced from ethanol through acetaldehyde in agreement with Eq. (1) but that acetaldehyde reacts to hemiacetal and further to ethyl acetate, which then hydrolyses to acetic acid in disagreement with Eq. (2). Based on our work it is assumed that acetic acid is produced primarily through the reaction of acetaldehyde with water over a Cu catalyst, which was also supported by Iwasa and Takezawa [7].

Breaking the conversions into elementary steps the likelihood of the suggested reaction pathway may be elucidated.

Table 1 shows a survey of elementary reactions established or proposed as parallels to elementary reactions for C1 conversions. Herein * signifies a free Cu surface site. The initial mechanism for the abstraction of hydrogen from ethanol to obtain acetaldehyde has been studied in the literature [8,11].

The initial conversion of ethanol to acetaldehyde is suggested to take place via steps I and II followed by another hydrogen abstraction step, see step III. Steps I and II in combination and step III were shown in temperature dependent ethanol adsorption studies (TDSS) on Cu/Cr₂O₃ by Colley et al. [11]. The dominant abstraction of α -hydrogen from adsorbed ethoxy on Cu in step III was confirmed by Chung et al. [8] by isotopic labelling.

As observed in our experiment acetaldehyde desorbes as an intermediate, step IV.

Furthermore, Colley et al. found that acetaldehyde easily dehydrogenates into acetyl, step V, and that acetyl reacts with ethoxy to ethyl acetate. Very small amounts of ethyl acetate were found in our work in the conversion of ethanol over Cu/SiO₂ indicating a low coverage of either ethoxy or acetyl. Assuming a considerable coverage of acetyl the reaction of an adsorbed acetyl with hydroxyl to CH₃COOH* may be suggested, step VI.

Iwasa and Takezawa [7] suggest the nucleophilic addition of water (OH) to adsorbed acetaldehyde as the pathway for acetic acid formation. They further made comparisons to the methanol system studied over Cu based catalysts and found several similarities. Therefore, in screening for more possible pathways inspiration has been found in the corresponding C1 system conversions, i.e. methanol (MeOH) reforming (MeOH + $H_2O = 3H_2 + CO_2$) or synthesis being catalysed on Cu surfaces in conjunction with the water gas shift reaction (CO + $H_2O = H_2 + CO_2$). Support to the valid comparison of the methanol and ethanol systems of reaction pathways over Cu catalyst may be found in a work by Shimada et al. [10] where the oxidation of formaldehyde and acetaldehyde, were studied. Chung et al. [8] expects analogies between ethanol and methanol dehydrogenation mechanisms due to their identical distance between the α -hydrogen and the oxygen under the consideration of configurational constraints.

The elementary reaction pathways for methanol and shift active Cu catalysts have been studied by Ovesen et al. [13] and Askgaard et al. [12]. In the C1 system, the elementary steps underlying the synthesis of methanol over Cu catalyst, where the side-product formaldehyde is found, is explained by the dissociation of adsorbed oxidised formaldehyde hydrate, H_2COO^* , on a free site to form HCHO^{*} and O^{*} by Askgaard et al. [12], the methanol synthesis taking place in a C1 system, while ethanol is a C2 compound. Thus, in the reverse direction, the oxidation of the adsorbed formaldehyde to the oxidised formaldehyde hydrate is implicitly suggested in the C1 system, and the further steps of its decomposition to H^{*} and adsorbed formate, and the final decomposition of formate to CO₂ and H₂ were verified at 470 K. As opposed to formate as a product in the C1 system acetate in the C2 system is a very stable compound which may easily be hydrogenated to acetic acid.

Following the suggested pathways for formaldehyde to formate by Askgaard et al. the formation of oxidised acetaldehyde hydrate CH_3CHOO^* is assumed possible, being the precursor to acetate and acetic acid.

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